

Synthesis and application of uracil derivatives as novel thermal stabilizers for rigid poly(vinyl chloride)

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ARTICLE INFO

Article history:

Received 18 June 2012

Received in revised form

23 October 2012

Accepted 14 November 2012

Available online 6 December 2012

Keywords:

Poly(vinyl chloride)

Thermal degradation

Stabilization

Organic thermal stabilizer

Uracil derivatives

Co-stabilizer

Synergistic effect

ABSTRACT

Novel uracil thermal stabilizers for rigid poly(vinyl chloride) (PVC), N, N-dimethyl-6-amino-uracil (DAU), N-monomethyl-6-amino-uracil (MAU) and N-monomethyl-6-amino-thiouracil (MATU) were synthesized successfully via a precipitation method, and characterized with ¹H NMR spectra. Evaluation of these compounds as thermal stabilizer for rigid PVC was measured by discoloration test, and also using Haake torque rheometer and TGA. The results showed that, these novel uracil derivatives exhibited greater stabilizing efficiency compared with traditional Ca/Zn stabilizers (CZ) and diphenylthiourea (DTU) with the same concentration in PVC mixtures. This is attributed to the ability of these compounds to replace the labile chlorine atoms in PVC chains, and absorb of HCl released by the degradation of PVC, which was proved by the FTIR and ¹H NMR spectral analysis. Furthermore, an excellent synergistic effect could be obtained when the model compound MATU combined with zinc stearate (ZnSt₂) in different mass ratios, and the initial color and long-term stability of PVC products were remarkably improved.

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1. Introduction

Thermal stabilizers play very important roles during the thermal processing of PVC because they must be incorporated to restrain the degradation of PVC whose decompose temperature is much lower than the processing temperature [1,2].

Thermal stabilizers realize the thermal stability mainly through absorption of hydrogen chloride (HCl) released by the degradation of PVC or replacing the labile chlorine atoms in PVC chains, such as allylic and tertiary chlorine atoms [3,4]. At present, lead salts [5], metal soaps [6], and organotin compounds [7] are the main kinds of PVC thermal stabilizers. However, they have obvious drawbacks in terms of toxicity, environmental pollution and low efficiency [8,9]. As a consequence, it has been highly desirable to explore an environmentally friendly stabilizer with non-toxicity and high efficiency.

Recently, the attention of many investigators has been focused on organic stabilizers [10–15]. For example, novel organic hydroxybenzylthioethers investigated by Peng Liu and coworkers [15], showed good efficiencies and exhibited synergistic effect with epoxidized soybean oil in stabilizing PVC. Sabaa et al. [16] developed a series of phenylurea and phenylthiourea derivatives and studied their efficiency to stabilize rigid PVC. They stated that these

nitrogen-containing compounds revealed high stabilizing potency for PVC and led to a true synergistic effect with metal soaps. But by far the application of organic stabilizers are limited due to their high cost and low efficiency. Hence, in the present study, a class of uracil derivatives, which are non-toxic and could be easily synthesized using urea derivatives as raw materials, were investigated by thermal characterization as novel organic thermal stabilizers or co-stabilizers for PVC.

2. Experimental

2.1. Materials

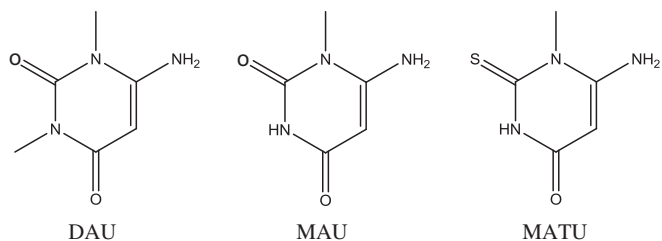
PVC (SG-5) used in this work was purchased from Xinjiang Tianye Group Co. Ltd., China. Calcium stearate, zinc stearate, dioctyl phthalate (DOP) and CaCO₃ (1000 mesh) were supplied by Zhejiang Himpton New Material Co. Ltd., China. Diphenylthiourea and all of the chemical reagents used in this study were obtained from Aladdin Reagent, China. All the reagents were used as received.

2.2. Preparation of uracil derivatives

Uracil derivatives were all prepared according to the following methods: 250 mL ethanol and sodium (11.5 g, 0.5 mol) were added to a 500-mL three-neck flask, equipped with a magnetic stirrer,

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Scheme 1. Structures of uracil derivatives.

a thermometer and a dropping funnel. The mixture was then stirred at room temperature. After 0.5 h, urea derivatives (0.25 mol) and ethyl cyanoacetate (26.5 mL, 0.25 mol) were added to the flask and the mixture was heated to 80 °C and refluxing for about 3 h. Finally, a 2 M HCl aqueous solution was added to the flask until the reaction mixture reached neutral. The resultant solid was separated by filtration, washed with deionized water and dried in a vacuum desiccator. The structures are shown in Scheme 1.

2.2.1. *N,N*-dimethyl-6-amino-uracil (DAU)

White solid, m.p. 303 °C, yield: 95.8%. ¹H NMR (DMSO): 6.78 (s, 2H, NH₂), 4.69 (s, 1H, CH), 3.24 (s, 3H, NCH₃), 3.07 (s, 3H, NCH₃).

2.2.2. *N*-monomethyl-6-amino-uracil (MAU)

Yellowish solid, m.p. 306 °C, yield: 93.2%. ¹H NMR (DMSO): 10.33 (s, 1H, NH), 6.78 (s, 2H, NH₂), 5.77 (s, 1H, CH), 3.17 (s, 3H, NCH₃).

2.2.3. *N*-monomethyl-6-amino-thiouracil (MATU)

White solid, m.p. 281 °C, yield: 96.7%. ¹H NMR (DMSO): 11.82 (s, 1H, NH), 7.00 (s, 2H, NH₂), 4.88 (s, 1H, CH), 3.68 (s, 3H, NCH₃).

Table 1
Thermal properties of uracil derivatives.

Stabilizers	DAU	MAU	MATU
Weight % at 200 °C	98	97	99
<i>T</i> _{10%} (°C)	299	330	285

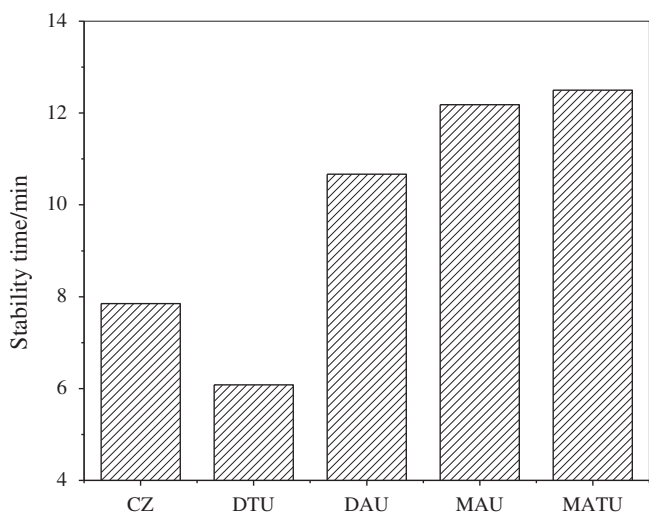


Fig. 1. Influences of the stabilizers (2 phr) on dynamic stability time of PVC at 180 °C.

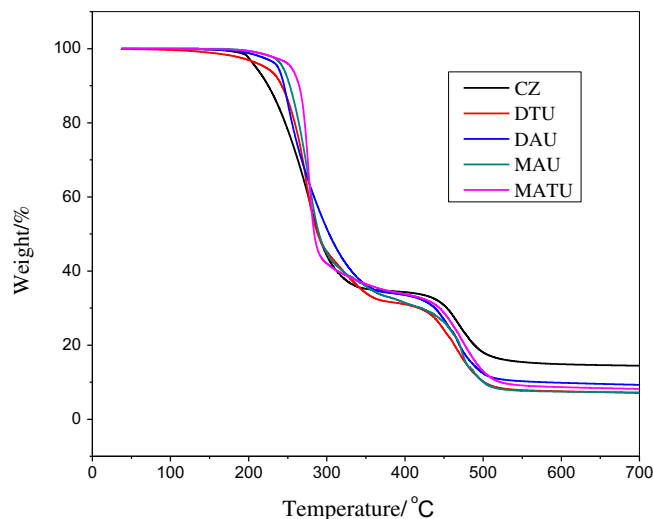


Fig. 2. Thermogravimetric analysis of PVC stabilized with CZ, DTU, DAU, MAU and MATU.

2.3. FTIR and ¹H NMR spectral analysis

The Fourier transform infrared (FTIR) spectra were obtained with a Nicolet FTIR 6700 infrared spectrophotometer, where the samples were prepared with KBr pellets. ¹H NMR spectra were measured on an ANANCE III (500 M) spectrometer, using DMSO-d₆ as solvent and tetramethylsilane (TMS) as the internal standard.

Table 2
TGA results of stabilized PVC.

Stabilizers	<i>T</i> _{onset} (°C)	<i>T</i> _{10%} (°C)	Weight loss at 200 °C (%)	Residue at 700 °C (%)
CZ	202	240	3	14
DTU	188	277	4	7
DAU	209	256	2	9
MAU	215	265	1	7
MATU	221	277	1	8

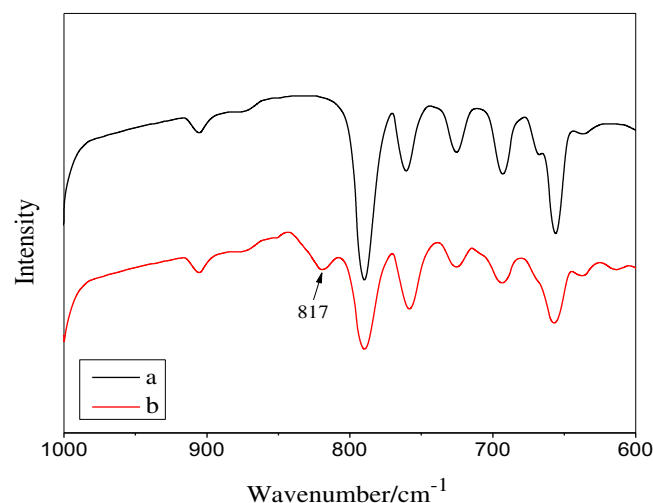


Fig. 3. IR spectra of MATU: (a) before treatment (b) treated under HCl gas condition at 180 °C for 2 h.

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